Method for Restructuring Keratin Fibers

This invention relates to a process for restructuring keratin fibers.

Nowadays, human hair is treated in many different ways with hair-care preparations. Such treatments include, for example, the cleaning of hair with shampoos, the care and regeneration of hair with rinses and conditioners and the bleaching, coloring and shaping of hair with coloring and tinting formulations, wave formulations and styling preparations. Among these, formulations for modifying or shading the color of the hair occupy a prominent position. The effect of this behavior is that hair is exposed in various ways to damaging influences which have an adverse effect on the surface structure.

Accordingly, there has been no shortage of attempts to counteract the damage done to the hair structure and to develop restructuring techniques. Various care components have been developed for specific use as aftertreatments for damaged hair. In addition, additional care components have been added to the hair treatment preparations, such as for example the hair fixing lotions used in permanent waving or hair colorants. For example, it was proposed in **DE-A1 196 17 569** that special amino acids be used as care components.

It has surprisingly been found that a distinctly increased restructuring of keratin fibers can be obtained by means of a totally new enzymatic process.

Restructuring in the context of the invention is understood to be a reduction in the damage done to keratin fibers by various influences. For example, restoring the natural strength of the hair plays an important role in this regard. Examples of damaging influences are, for example, permanent wave treatments, oxidative coloring or lightening of the hair and frequent washing, blow drying and combing. Damage can also be done by

environmental influences, such as UV light for example. Restructured fibers are distinguished, for example, by improved luster, by improved feel and by easier combability. In addition, successful restructuring can be physically manifested as an increase in melting point by comparison with damaged fibers.

In a first embodiment, therefore, the present invention relates to a process for restructuring keratin fibers in which (A) at least one enzyme of the transglutaminase type and (B) at least one active substance with substrate activity for the enzyme are applied to the fibers.

Besides the restructuring of damaged fibers, a second objective of the present invention was to obtain a hair-setting effect for undamaged hair. Accordingly, the process according to the invention may also be used for setting the hair for special styling effects.

Keratin fibers in the context of the invention are understood to include pelts, wool, feathers and in particular human hair.

An enzyme which is preferably used in the process according to the invention is transglutaminase (official name: protein glutamine gamma-glutamyltransferase; EC 2.3.2.13). This enzyme preferentially catalyzes the reaction of the amino acid moiety glutamine in a protein with an alkylamine to form an N5-alkylglutamine protein with release of ammonia. A preferred natural alkylamine which plays a role in this reaction is the amino acid lysine or the amino acid moiety lysine in a protein.

In principle, any enzymes with transglutaminase activity are suitable for carrying out the present invention. Suitable enzymes of this type are, for example, transglutaminases obtained from guinea pig liver, *Physarum polycephalum*, *Medicago savica* or *Bacillus subtilus*. The calcium-independent transglutaminases described, for example, in **EP 726 317 A2** and in **EP 397 606 A1** which are marketed by Ajinomoto are particularly preferred. The Ajinomoto products Activa® WM and EB are preferred, Activa® WM being particularly preferred.

The use of transglutaminases in cosmetic formulations is already known from the literature. For example, **US 5,490,980** describes a composition for treating human skin, hair or nails with which active substances containing a primary amino group are added onto the glutamine components of the skin, hair or nails by transglutaminase. However, there is nothing in this document which points to the subject of the present invention or to the restructuring properties of this process.

In the context of the invention, an active substance with substrate activity is any substance which can be added onto the hair by the transglutaminase. This can be done, for example, by crosslinking the active substances with substrate activity with one another, i.e. by forming a kind of membrane around the hair. However, this can also be done with advantage by covalent bonding of the active substances with substrate activity to the lysine and/or glutamine components of the hair.

In a first preferred embodiment of the present invention, naturally occurring substances are used as active substances with substrate activity. Proteins, protein hydrolyzates and derivatives thereof are particularly suitable for this purpose. Protein hydrolyzates are product mixtures obtained by acid-, base- or enzyme-catalyzed degradation of proteins.

According to the invention, proteins and protein hydrolyzates of both vegetable and animal origin may be used.

Animal proteins are, for example, elastin, collagen, keratin, silk and milk protein. Examples of proteins of vegetable origin are soya, almond, pea, alga, potato and wheat protein.

Although proteins as such are preferably used, other natural active substances with substrate activity, such as for example peptides, amino acids and corresponding derivatives, may also be used instead. Derivatives of the protein hydrolyzates, for example in the form of their fatty acid condensation products or cationic derivatives, may also be used but are less preferred.

Casein, soya protein and wheat protein are particularly preferred, casein being most particularly preferred.

In a second preferred embodiment of the invention, substances synthetically functionalized with an H_2N-R group or an H_2N-(CO)-R' group, where R and R' stand for an unbranched C_{1-8} alkylene group, are used as active substances with substrate activity. Particularly preferred functional groups are the groups H_2N-$(CH_2)_4$ and H_2N-(CO)-CH_2-CH_2- derived from lysine or glutamine.

In addition, monomers such as, for example, lysine and glutamine may be used in accordance with the invention as active substances with substrate activity. They may be used both as an additional active substance with substrate activity and as sole component. In a preferred embodiment of the invention, both proteins and corresponding monomers may be used during the process to improve fastness to washing by fairly rapidly building up a dense network of the active substances with substrate activity.

The active substances with substrate activity are present in the preparations used in accordance with the invention in quantities of preferably 0.005 to 10% by weight, based on the composition as a whole. Quantities of 0.01 to 2% by weight are particularly preferred. The ratio by weight of the transglutaminase type enzyme to the active substance with substrate activity is preferably 1:4000 to 1:1 and more preferably 1:2000 to 1:50.

So far as the time sequence of the process is concerned, the invention is not subject to any limitations. It is possible in principle to apply two separate preparations containing (a) the active substance with substrate activity and (b) the transglutaminase type enzyme successively in any order to the fibers. In a preferred embodiment, the two components (a) and (b) are applied to the fibers in that order. According to the invention, the components may also be separately applied in the order (b) $\rightarrow$ (a). In

this case, however, the time interval between steps (a) and (b) should not be too long to ensure that the fibers do not dry between the steps.

Although this two-stage process does produce the desired effects, it may be preferred to carry out the process according to the invention in a single stage because single-stage processes are easier to carry out. The active substance with substrate activity may be applied together with the enzyme preparation. In a preferred embodiment of the invention, the two components are mixed immediately before application.

Although in principle the preparation can remain on the hair, a preferred embodiment of the process according to the invention is characterized in that the preparation containing the enzyme is rinsed out after a contact time of 3 to 120 minutes. The preparation may be rinsed out with clean water. Contact times of 15 to 30 minutes have proved to be sufficient in most cases.

Irrespective of the course of the process according to the invention, it has proved to be of advantage to apply the enzyme preparation at a temperature of 20 to 55°C and more particularly at a temperature of 35 to 50°C.

In principle, there are no limits to the nature of the enzyme preparation. According to the invention, aqueous, alcoholic and oily preparations and mixtures thereof are particularly suitable. Aqueous preparations are particularly preferred. These may be, for example, solutions, dispersions, emulsions (water-in-oil emulsions, oil-in-water emulsions and multiple emulsions and PIT emulsions). The pH value of these preparations is generally in the range from 2 to 10, preferably in the range from 4 to 9 and more preferably in the range from 6 to 8.

In a preferred embodiment of the present invention, the enzyme preparations are formulated as a thickened solution. To this end, the preparations are thickened with thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed

gums, dextrans, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrins, clays, for example bentonite, or fully synthetic hydrocolloids, for example polyvinyl alcohol or even polyacrylic acid polymers. In a preferred embodiment, the enzyme preparations are formulated with low viscosities.

Besides the enzyme and optionally the active substance with substrate activity, the enzyme preparations may contain all the usual constituents suitable for the treatment of keratin fibers, particularly human hair. Aqueous preparations are preferred. Aqueous preparations in the context of the invention are preparations which contain at least 50% by weight water, based on the preparation as a whole.

It has proved to be of advantage for the enzyme preparation to contain at least one surfactant. Suitable surfactants are both anionic, ampholytic, zwitterionic or nonionic surfactants and cationic surfactants. If necessary, the expert may carry out simple preliminary tests to determine whether the various surfactants have any effect on the activity of the transglutaminase type enzyme.

A preferred embodiment of the invention is characterized by the use of a combination of anionic and nonionic surfactants or a combination of anionic and amphoteric surfactants.

Claim 5

However, it has proved to be of advantage in individual cases to select the surfactants from amphoteric or nonionic surfactants because they generally have less influence on the coloring process according to the invention.

Suitable anionic surfactants in the preparations according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22

carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide and hydroxyl groups may also be present in the molecule.

Nonionic surfactants contain, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C_{12-22} fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide to glycerol,
- C_{8-22} alkyl mono- and oligoglycosides and ethoxylated analogs thereof and
- products of the addition of 5 to 60 moles of ethylene oxide to castor oil and hydrogenated castor oil.

Preferred nonionic surfactants are alkyl polyglycosides corresponding to the general formula $R^1O-(Z)_x$. These compounds are characterized by the following parameters.

The alkyl group R^1 contains 6 to 22 carbon atoms and may be both linear and branched. Primary linear and 2-methyl-branched aliphatic groups are preferred. Such alkyl groups are, for example, 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl. 1-Octyl, 1-decyl, 1-lauryl and 1-myristyl are particularly preferred. Where so-called "oxo alcohols" are used as starting materials, compounds with an odd number of carbon atoms in the alkyl chain predominate.

The alkyl polyglyosides suitable for use in accordance with the invention may, for example, contain only one particular alkyl group R^1. However, such compounds are normally prepared from natural fats and oils or mineral oils. In this case, mixtures corresponding to the starting

compounds or corresponding to the particular working up of these compounds are present as the alkyl groups R.

Particularly preferred alkyl polyglycosides are those in which R^1 consists

- essentially of C_8 and C_{10} alkyl groups,
- essentially of C_{12} and C_{14} alkyl groups,
- essentially of C_8 to C_{16} alkyl groups or
- essentially of C_{12} to C_{16} alkyl groups.

Any mono- or oligosaccharides may be used as the sugar unit Z. Sugars containing 5 or 6 carbon atoms and the corresponding oligosaccharides are normally used. Examples of such sugars are glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. Preferred sugar units are glucose, fructose, galactose, arabinose and sucrose; glucose is particularly preferred.

The alkyl polyglycosides suitable for use in accordance with the invention contain on average 1.1 to 5 sugar units. Alkyl polyglycosides with x values of 1.1 to 1.6 are preferred. Alkyl glycosides where x is 1.1 to 1.4 are most particularly preferred.

Besides acting as surfactants, the alkyl glycosides may also be used to improve the fixing of perfume components to the hair. Accordingly, in cases where the effect of the perfume oil on the hair is intended to last longer than the duration of the hair treatment, alkyl glycosides will preferably be used as another ingredient of the preparations according to the invention.

Alkoxylated homologs of the alkyl polyglycosides mentioned may also be used in accordance with the invention. These homologs may contain on average up to 10 ethylene oxide and/or propylene oxide units per alkyl glycoside unit.

Zwitterionic surfactants may also be used, particularly as co-surfactants. In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one $-COO^{(-)}$ or $-SO_3^{(-)}$ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinates, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinates, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Also suitable, particularly as co-surfactants, are ampholytic surfactants. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8-18} alkyl or acyl group, contain at least one free amino group and at least one -COOH or $-SO_3H$ group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl aminopropionate, cocoacyl aminoethyl aminopropionate and C_{12-18} acyl sarcosine.

According to the invention, the cationic surfactants used are particularly those of the quaternary ammonium compound, esterquat and amidoamine type.

Preferred quaternary ammonium compounds are ammonium halides, more particularly chlorides and bromides, such as alkyl trimethyl

ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride and the imidazolium compounds known under the INCI names of Quaternium-27 and Quaternium-83. The long alkyl chains of the above-mentioned surfactants preferably contain 10 to 18 carbon atoms.

Esterquats are known substances which contain both at least one ester function and at least one quaternary ammonium group as structural element. Preferred esterquats are quaternized ester salts of fatty acids with triethanolamine, quaternized ester salts of fatty acids with diethanol alkylamines and quaternized ester salts of fatty acids with 1,2-dihydroxypropyl dialkylamines. Such products are marketed, for example, under the names of Stepantex®, Dehyquart® and Armocare®. The products Armocare® VGH-70, an N,N-bis-(2-palmitoyloxyethyl)-dimethyl ammonium chloride, and Dehyquart® F-75 and Dehyquart® AU-35 are examples of such esterquats.

The alkyl amidoamines are normally prepared by amidation of natural or synthetic fatty acids and fatty acid cuts with dialkyl aminoamines. A compound from this group particularly suitable for the purposes of the invention is the stearamidopropyl dimethylamine obtainable under the name of Tegoamid® S 18.

The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with different alkyl chain lengths dependent upon the particular raw material are obtained.

The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products

may be both products with a "normal" homolog distribution and products with a narrow homolog distribution. Products with a "normal" homolog distribution are mixtures of homologs which are obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

In addition, the enzyme preparations used in accordance with the invention preferably contain at least one oil component.

Oil components suitable for the purposes of the invention are, in principle, any water-insoluble oils and fatty compounds and mixtures thereof with solid paraffins and waxes. According to the invention, water-insoluble substances are defined as substances of which less than 0.1% by weight dissolves in water at 20°C. The melting point of the individual oil or fatty components is preferably below about 40°C. Oil and fatty components which are liquid at room temperature, i.e. below 25°C, can be particularly preferred for the purposes of the invention. However, where several oil and fatty components and optionally solid paraffins and waxes are used, it is generally sufficient if the mixture of the oil and fatty components and optionally paraffins and waxes satisfies these requirements.

A preferred group of oil components are vegetable oils. Examples of such oils are sunflower oil, olive oil, soya oil, rapeseed oil, almond oil, jojoba oil, orange oil, wheatgerm oil, peach kernel oil and the liquid fractions of coconut oil.

However, other triglyceride oils, such as the liquid fractions of bovine tallow, and synthetic triglyceride oils are also suitable.

Another group of compounds particularly preferred for use as oil

components in accordance with the invention are liquid paraffin oils and synthetic hydrocarbons and di-n-alkyl ethers containing a total of 12 to 36 carbon atoms and, more particularly, 12 to 24 carbon atoms, such as for example di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether, di-n-dodecyl ether, n-hexyl-n-octyl ether, n-octyl-n-decyl ether, n-decyl-n-undecyl ether, n-undecyl-n-dodecyl ether and n-hexyl-n-undecyl ether and ditert.butyl ether, diisopentyl ether, di-3-ethyldecyl ether, tert.butyl-n-octyl ether, isopentyl-n-octyl ether and 2-methylpentyl-n-octyl ether. The compounds 1,3-di-(2-ethylhexyl)-cyclohexane and di-n-octyl ether obtainable as commercial products (Cetiol® S and Cetiol® OE, respectively) can be preferred.

Other oil components suitable for use in accordance with the invention are fatty acid and fatty alcohol esters. The monoesters of fatty acids with alcohols containing 3 to 24 carbon atoms are preferred. This group of substances are products of the esterification of fatty acids containing 8 to 24 carbon atoms such as, for example, caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof obtained, for example, in the pressure hydrolysis of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerization of unsaturated fatty acids with alcohols such as, for example, isopropyl alcohol, caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure

hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. According to the invention, isopropyl myristate, isononanoic acid C_{16-18} alkyl ester (Cetiol® SN), stearic acid-2-ethylhexyl ester (Cetiol® 868), cetyl oleate, glycerol tricaprylate, cocofatty alcohol caprate/caprylate and n-butyl stearate are particularly preferred.

Other oil components suitable for use in accordance with the invention are dicarboxylic acid esters, such as di-n-butyl adipate, di-(2-ethylhexyl)-adipate, di-(2-ethylhexyl)-succinate and diisotridecyl acelate, and diol esters, such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol di-(2-ethylhexanoate), propylene diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate, and also complex esters, for example diacetyl glycerol monostearate.

Finally, fatty alcohols containing 8 to 22 carbon atoms may also be used as oil components in accordance with the invention. The fatty alcohols may be saturated or unsaturated and linear or branched. Examples of fatty alcohols suitable for use in accordance with the invention are decanol, octanol, octenol, dodecenol, decenol, octadienol, dodecadienol, decadienol, oleyl alcohol, erucyl alcohol, ricinolyl alcohol, stearyl alcohol, isostearyl alcohol, cetyl alcohol, lauryl alcohol, myristyl alcohol, arachidyl alcohol, capryl alcohol, capric alcohol, linoleyl alcohol, linolenyl alcohol and behenyl alcohol and Guerbet alcohols thereof (this list is purely exemplary and is not intended to limit the invention in any way). However, the fatty alcohols emanate from preferably natural fatty acids, normally being obtained from the esters of the fatty acids by reduction. According to the invention, it is also possible to use the fatty alcohol cuts which are produced by reduction of naturally occurring triglycerides, such as bovine tallow, palm oil, peanut oil, rapeseed oil, cottonseed oil, soybean

oil, sunflower oil and linseed oil, or fatty acid esters formed from the transesterification products thereof with corresponding alcohols and which therefore represent a mixture of different fatty alcohols.

In a preferred embodiment, the enzyme preparations used in accordance with the invention contain a care component. This care component is preferably selected from cationic polymers and silicones.

A first group of cationic polymers are the so-called "temporarily cationic" polymers. These polymers normally contain an amino group which is present as a quaternary ammonium group and hence cationically at certain pH values.

Among the cationic polymers, the permanently cationic polymers are preferred. According to the invention, "permanently cationic polymers" are polymers which contain a cationic group irrespective of the pH of the composition. These are generally polymers which contain a quaternary nitrogen atom, for example in the form of an ammonium group. Preferred cationic polymers are, for example,

- the quaternized cellulose derivatives commercially available under the names of Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and Polymer JR® 400 are preferred quaternized cellulose derivatives,
- polysiloxanes containing quaternary groups such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning® 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, Quaternium-80),
- cationic guar derivatives such as, in particular, the products marketed under the names of Cosmedia® Guar and Jaguar®,

- polymeric dimethyl diallyl ammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid. The products commercially available under the names of Merquat® 100 (poly(dimethyl diallylammonium chloride)) and Merquat® 550 (dimethyl diallylammonium chloride/acrylamide copolymer) are examples of such cationic polymers,
- copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate such as, for example, vinyl pyrrolidone/dimethylamino methacrylate copolymers quaternized with diethyl sulfate. Such compounds are commercially available under the name of Gafquat® 734 and Gafquat® 755,
- The vinyl pyrrolidone/vinyl imidazolinium methochloride copolymers commercially available under the name of Luviquat® FC 370, FC 550, FC 905 and HM 552,
- quaternized polyvinyl alcohol and
- the polymers containing quaternary nitrogen atoms in the main polymer chain known under the names of Polyquaternium 2, Polyquaternium 17, Polyquaternium 18 and Polyquaternium 27.

Other suitable cationic polymers are the polymers known by the names of Polyquaternium-24 (commercial product: Quatrisoft® LM 200 for example), Polyquaternium-32, Polyquaternium-35 and Polyquaternium-37 (commercial products: Salcare® SC 92 and Salcare® SC 95). Also suitable for use in accordance with the invention are the vinyl pyrrolidone copolymers known by the commercial names of Copolymer 845 (manufacturer: ISP), Gaffix® VC 713 (manufacturer: ISP), Gafquat® ASCP 1011, Gafquat® HS 110, Luviquat® 8155 and Luviquat® MS 370.

According to the invention, preferred cationic polymers are quaternized cellulose derivatives, polymeric dimethyl diallyl ammonium salts, Polyquaternium 27 and copolymers thereof and polymers of the Polyquaternium 2 type. Cationic cellulose derivatives, more particularly the

commercial product Polymer® JR 400, and polymers of the Polyquaternium 2 type, more particularly the commercial product Mirapol® A-15, are most particularly preferred cationic polymers.

The cationic polymers are present in the preparations used in accordance with the invention in quantities of preferably 0.05 to 5% by weight, based on the preparation as a whole. Quantities of 0.1 to 5% by weight are particularly preferred.

Amphopolymers may also be used as a care component in combination with or alternatively to the cationic polymers. Amphopolymers are amphoteric polymers, i.e. polymers which contain both free amino groups and free -COOH or $-SO_3H$ groups in the molecule and which are capable of forming inner salts, zwitterionic polymers which contain quaternary ammonium groups and $-COO^-$ or $-SO_3^-$ groups in the molecule and polymers which contain –COOH- or SO_3H groups and quaternary ammonium groups. One example of an amphopolymer suitable for use in accordance with the invention is the acrylate resin commercially available as Amphomer® which is a copolymer of tert.butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)-acrylamide and two or more monomers from the group consisting of acrylic acid, methacrylic acid and simple esters thereof. Other preferred amphopolymers consist of unsaturated carboxylic acids (for example acrylic and methacrylic acid), cationically derivatized unsaturated carboxylic acids (for example acrylamidopropyl trimethyl ammonium chloride) and optionally other ionic or nonionic monomers of the type disclosed, for example, in **DE-OS 39 29 973** and the prior art literature cited therein. According to the invention, terpolymers of acrylic acid, methyl acrylate and methacrylamidopropyl trimonium chloride, which are commercially available under the name of Merquat® 2001 N, and the commercial product Merquat® 280 are particularly preferred ampho-polymers.

Other care substances suitable for use in accordance with the

invention are silicone oils and silicone gums, more particularly dialkyl and alkylaryl siloxanes such as, for example, dimethyl polysiloxane and methylphenyl polysiloxane and alkoxylated and quaternized analogs thereof. Examples of such silicones are the products marketed by Dow Corning under the names of DC 190, DC 200 and DC 1401 and the commercial products DC 344 and DC 345 of Dow Corning, Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning® 929 emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil® Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80) and the commercial product Fancorsil® LIM-1. A suitable anionic silicone oil is the product Dow Corning® 1784.

Besides the transglutaminase type enzyme and the other preferred components mentioned above, the enzyme preparations may basically contain any other components known to the expert for such cosmetic preparations.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- structurants, such as maleic acid and lactic acid,
- hair-conditioning compounds, such as phospholipids, for example soybean lecithin, egg lecithin and kephalins,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- fiber structure improvers, more particularly mono-, di- and oligosaccharides such as, for example, glucose, galactose, fructose and lactose,

- quaternized amines, such as methyl-1-alkylamidoethyl-2-alkylimidazolinium methosulfate,
- defoamers, such as silicones,
- dyes for coloring the composition,
- antidandruff agents, such as Piroctone Olamine, Zinc Omadine and Climbazol,
- sun protection factors, more particularly derivatized benzophenones, cinnamic acid derivatives and triazines,
- substances for adjusting the pH value, such as for example the usual acids, more particularly edible acids and bases,
- active principles, such as allantoin, pyrrolidone carboxylic acids and salts thereof and bisabolol,
- vitamins, provitamins and vitamin precursors, more particularly those of groups A, B_3, B_5, B_6, C, E, F and H,
- plant extracts, such as the extracts of green tea, oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, hawthorn, lime blossom, almond, aloe vera, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, ginseng and ginger root ,
- cholesterol,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax and paraffins,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA, β-alanine diacetic acid and phosphonic acids,
- swelling and penetration agents, such as glycerol, propylene glycol

monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates,

- opacifiers, such as latex, styrene/PVP and styrene/acrylamide copolymers,
- pearlizers, such as ethylene glycol mono- and distearate and PEG-3-distearate,
- pigments,
- stabilizers for hydrogen peroxide and other oxidizing agents,
- propellents, such as propane/butane mixtures, N_2O, dimethyl ether, CO_2 and air.

Information on other optional components and the quantities in which they are used can be found in the reference books known to the expert, for example Kh. Schrader, **Grundlagen und Rezepturen der Kosmetika, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989.**

In a second embodiment, the present invention relates to the use of (A) at least one enzyme of the transglutaminase type and (B) at least one active substance with substrate activity for the enzyme for restructuring keratin fibers.

In a third embodiment, the present invention relates to the use of (A) at least one enzyme of the transglutaminase type and (B) at least one active substance with substrate activity for the enzyme for setting keratin fibers.

In a fourth embodiment, the present invention relates to a two-part kit for restructuring keratin fibers which contains a first preparation containing (a) an active substance with substrate activity and a second composition containing (b) an enzyme of the transglutaminase type.

The following Examples are intended to illustrate the invention.

Examples

a) Pretreatment

Alkinco tresses (0.5 g, Code 6634) were subjected to a conventional permanent wave treatment with the commercial product "Poly Lock-Normale Dauerwelle". In the first step of this permanent wave treatment, the fibers were exposed to the reducing solution (containing 7.9% by weight thioglycolic acid) for 40 minutes at room temperature, rinsed with clean water and then fixed for 10 minutes at room temperature (oxidizing solution containing 2.6% by weight of hydrogen peroxide). After the oxidative treatment, the fibers were rinsed and dried.

b) Aftertreatment

Test 1): aftertreatment according to the invention

The tresses were immersed for 60 minutes at a temperature of 50°C in 2 ml of an aqueous casein solution (30 mg/ml, adjusted to pH 7.6 with tris(hydroxymethyl)aminomethane (TRIS) HCl buffer) to which 100 µl of an aqueous transglutaminase solution (50 mg/ml Activa® WM[1], corresponding to 0.5 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer) had been added.

[1] powder form commercial product, 1% by weight transglutaminase in 99% by weight dextrin

Test 2): aftertreatment with casein

The tresses were immersed for 60 minutes at a temperature of 50°C in 2 ml of an aqueous casein solution (30 mg/ml, adjusted to pH 7.6 with tris(hydroxymethyl)aminomethane (TRIS) HCl buffer)

Test 3): aftertreatment with transglutaminase

The tresses were immersed for 60 minutes at a temperature of 50°C in 2 ml of an aqueous transglutaminase solution (1.2 mg/ml Activa® WM,

corresponding to 0.012 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer).

c) Determination of the hair-structuring effect by HP-DSC

The following melting points were determined by DSC analysis (Perkin Elmer DSC-7):

	Mean value in °C	Scatter
Test 1)	148.24	0.40
Test 2)	147.91	0.07
Test 3)	147.77	0.18
Test 4) Tresses with no aftertreatment	147.62	0.02

Statistical evaluation by a two-sided heterogeneous T-Test revealed a significance of 99.73% between the measured values of tests 1) and 2).